

Energetic, electronic and magnetic properties of Mn-dimers on reconstructed (001) GaAs surfaces.

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We study energetic, magnetic, and electronic properties of diluted substitutional Mn-pairs on the reconstructed (001) GaAs surfaces. The studies are based on first-principles calculations in the framework of the density functional theory. We demonstrate that the stability of the systems strongly depends on the position, orientation, and the distance between the Mn-atoms constituting the pair. Independently of the considered surface reconstruction pattern, the Mn-pairs with Mn-atoms being the nearest neighbors on cationic sublattice (hereafter named dimers) turn out to be energetically more favorable than the pairs with the larger distance between the Mn-atoms. However, the preferential build-up orientation of the Mn-dimer depends on the surface reconstruction and is parallel either to $[110]$ or $[\bar{1}\bar{1}0]$ crystallographic direction. We reveal also the mechanisms of the magnetic ordering of Mn-dimers. The Mn-dimers along the $[110]$ crystallographic direction exhibit always ferromagnetic alignment of Mn spins, whereas the spins in the Mn-dimers along $[\bar{1}\bar{1}0]$ direction are mostly anti-ferromagnetically aligned. In the electronic structure of the systems containing Mn-dimers with ferromagnetically aligned spins, we observe the valence band hole states in the neighborhood of Fermi energy. This indicates that the surface ferromagnetism in this prototype of dilute magnetic semiconductors can be explained in terms of the p - d Zener model.

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I. INTRODUCTION

Nowadays, the epitaxially grown semiconducting magnetic films like (Ga,Mn)As have attracted great deal of attention, mostly due to its considerable properties that make them promising candidates for spintronic applications^{1,2}. It has been experimentally shown that properties of these materials depend strongly on how the magnetic ions are incorporated into the host, for example, interstitial Mn-ions reduce the Curie temperature and the hole concentration, and hence, hinder ferromagnetism. Moreover, the existence of the preferential build-up direction of Mn-dimers along the crystallographic direction onto (001) GaAs surface results in a bulk uniaxial magnetic anisotropies (in-plane and out-of-plane); as it has been theoretically shown by the authors³. In Ref.³, the preferential build-up direction of Mn-dimers has been ascribed to the growth mechanism of (Ga,Mn)As and the manner the Mn-pairs incorporate into the GaAs surface. The uniaxial magnetic anisotropy in systems is of crucial importance for design of novel spintronics devices⁴. Furthermore, it has been recently reported that a single atom substitution technique, with spectroscopic imaging in a scanning tunneling microscope (STM), opens a new way to manipulate atom by atom at the surface⁵, and therefore, the surface magnetism. To control the location

of Mn in (Ga,Mn)As, it is crucial to understand the initial incorporation processes of Mn-pairs onto the surfaces of host GaAs. So far, theoretical approaches reported, by using the empirical in nature self-consistent Hückel method and a cluster model, that the Mn-atoms prefer to be substituted at the surface Ga-atoms instead of being adsorbed above them⁶. Recently, the density functional theory (DFT) based calculations demonstrated that the interstitial Mn is easily incorporated beneath the As-As dimer on the (001) GaAs surface⁷. Then, Zhang *et al.*⁸ have shown that the stability of several types of structures induced by the Mn adsorption depends on the stoichiometry of the surface composition. Very recently the combined DFT calculations (under the equilibrium conditions of growth) and experimental works have demonstrated⁹ that Mn-atoms prefer to substitute Ga-sites at a subsurface layer under the As-rich conditions for (001) GaAs oriented surface, whereas interstitial sites are preferable under Ga-rich conditions. Moreover, the preferable incorporation of Mn-ions in the substitutional site in GaAs under As-rich conditions had been predicted before by Zunger¹⁰. Therefore, to get an overall understanding of the Mn incorporation mechanisms on the (001) GaAs surface, and facilitate comparison between various surface geometries, we have performed extensive studies of all possible non-equivalent substitutional po-

sitions of the Mn-pairs onto (001) reconstructed GaAs surfaces: (2×1) , $\beta(2 \times 4)$, $\beta 2(2 \times 4)$, under As-rich conditions, employing the identical computational tool.

In addition, the magnetism of differently oriented surfaces, in general, and theirs reconstructions, in particular, are only very weakly understood quantitatively up to now. Strandberg et al.¹¹ studied the Mn-pairs at different crystallographic orientations at (110) GaAs surface by employing the Kinetic Tight Binding model. They showed that the long-range interactions were anisotropic in terms of orientations and distances between the Mn-pairs. They also demonstrated that the magnetic ions prefer to be ferromagnetically arranged. The anisotropic character of the effective exchange constant for the Mn-pairs differently oriented at (110) surface has been shown in Ref.¹², by using the Density Functional method. Both papers studied the most common cleaved surface employed in cross sectional STM studies (although this is not the most common GaAs growth surface, which is the (001)). In the literature, there is lack of information about the exchange interaction between the magnetic ions (in dilute regime) placed onto the experimentally observed reconstructed (001) GaAs surfaces.

Detailed knowledge of the magnetic interactions at the reconstructed surfaces is essential for fabricating new high speed spintronics devices. Therefore, in this work we investigate magnetic properties of substitutional positions of Mn-dimers onto the differently reconstructed (001) GaAs surfaces in diluted case. Moreover, we report the role of the surface reconstruction in the Mn incorporation process. We also examine the energetic properties and stability of Mn-GaAs surfaces. The paper is organized as follows. In section 2, we present computational details. Section 3 contains the results of the studies and section 4 conclusions of the work.

II. COMPUTATIONAL DETAILS

The calculations are performed within the DFT^{13,14} computational scheme employing the L(S)DA+U approach and parameterization of the exchange-correlation functional provided by Ceperly and Adler (CA)¹⁵, as it is implemented in SIESTA code¹⁶. The electron ion-core interactions are represented by norm-conserving pseudopotentials of the Troullier-Martins type¹⁷ with non-linear core corrections¹⁸. The electron wave-functions are expanded into a flexible multiple centered atom basis set of numerical atomic orbitals¹⁹. In the calculations we use double- ζ for the s and p shells of any element and a triple- ζ basis set for the Mn $3d$ shell. The cutoff of 300 Ry is used for the real space mesh. The Brillouin Zone (BZ) integration is performed by means of the k-grid parameter of 30 Å. These parameters have been chosen to provide sufficient accuracy of the surface energy, being not worse than 0.05 meV/Å². For L(S)DA+U calculations, we adopted the value of the U parameter equal to 4.5 eV for Mn $3d$ states, which is in perfect agreement

with the previous photoemission data²⁰, and consistent with previous L(S)DA+U calculations for the bulk^{21,22}.

In order to get a set of reasonably optimized parameters controlling the computational run of the surface calculations, we have made the careful tests, which guarantee simultaneously the required accuracy and high efficiency of the very demanding computations. We attempt to evaluate systematic errors of the performed calculations. In particular, we are interested in energetics of the surface calculations, therefore, the convergence in terms of the surface free energy is checked. Our calculation accuracy of the surface free energy is not smaller than 0.37 [meV/Å²], which is quite accurate, if one compares this value with the typical values of the surface energy for GaAs(001), which are in between 40 to 100 [meV/Å²]²³.

A. Model of a surface

In order to investigate the physical properties of substitutional isolated Mn-pairs on the GaAs(001) surfaces, we used supercell geometry and construct the slab system as it is presented in Fig. 1. To model (001) GaAs

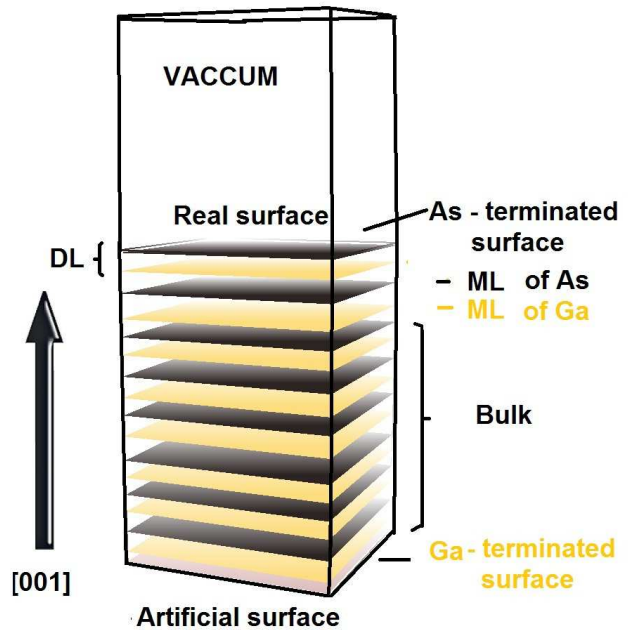


FIG. 1. The schematic diagram of the supercell used in the calculations. The supercell consists of 8 double layers of As-Ga. Each monolayer contains 16 atoms. The artificial surface denotes the surface with hydrogen saturated dangling bonds, which mimics the bulk type of bindings.

surface, 8 double As-Ga layers (DLs) lying in the (001) crystallographic planes are used. The GaAs crystal is represented by a standard zinc blende (zb) cell with calculated lattice parameter equal to 5.639 Å, which is in good agreement with experimental value of 5.648 Å²⁴. If the slab is not thick enough, the dangling bond states on

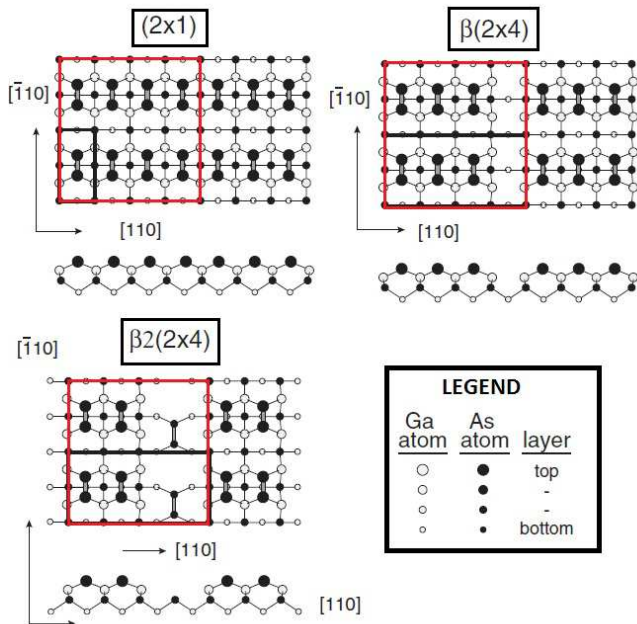


FIG. 2. The top-view and side-view schematic diagrams of (001) GaAs reconstructed surfaces under As-rich conditions used in this work. On the surface, As-As dimerization along $[\bar{1}10]$ direction is clearly visible. Four monolayers from the top of the slab are shown. Positions in the uppermost atomic layers are indicated by larger symbols. The black and white balls indicate the arsenic and gallium atoms, respectively. The rectangular, red line denotes the lateral supercell chosen for the calculations.

the two sides of the slab might interact with each other and give rise to artificial charge transfer from top surface of the slab to its bottom. To avoid this effect and decouple the two sides of the slab, we saturate the dangling bonds from the bottom side of the slab by a monolayer of pseudo-Hydrogen atoms with fractional charge equal to $Z = 1.25$. Each of the Ga-atom is saturated by two pseudo-atoms, to mimic the bulk types of bonds. In order to simulate independent crystal surface, 16 Å of vacuum is added (it corresponds to 12 MLs of the bulk crystal), with the slab dipole correction option enabled as it is implemented in SIESTA code¹⁶.

We consider experimentally observed reconstructed (001) GaAs surfaces under As-rich conditions: $\beta(2 \times 4)$ ²⁵, $\beta 2(2 \times 4)$ ^{26–29}, and also theoretically proposed (2×1) reconstruction^{30,31}, which are presented in Fig. 2. All of the atoms in pure surfaces are fully relaxed until the maximal force on each atom reaches the value of 0.02 eV/Å. These surfaces are our starting points for further calculations.

To investigate the physical properties of isolated Mn-pairs (it models properly diluted case), we substitute two Ga-atoms by two Mn-atoms at the top most monolayer of Ga-atoms at pure (001) GaAs reconstructed surfaces. Our simulated supercells contain 288 atoms for (2×1) ,

284 atoms for $\beta(2 \times 4)$, and 276 atoms for $\beta 2(2 \times 4)$ reconstructed surface. Each of the monolayer comprises 16 atoms, making the Mn-coverage of the layer equal to 1/8. The surface area corresponds to the lateral (4×4) cell of the dimensions $16\text{Å} \times 16\text{Å}$. During the optimization procedure 6 MLs from the top of the slab are fully relaxed, whereas the bottom of the slab is fixed to reflect the bulk character of this part of the supercell.

III. RESULTS

Here we present main results of our studies. First, we describe the energetic issues in subsection 3.1, and then we turn to the electronic and magnetic properties of the surfaces with adsorbed Mn-pairs in subsection 3.2.

A. Energetics

In this section, we focus on structural and energetic properties from the standpoint of the different possible incorporations of Mn-pairs which are embedded onto cationic sublattice into the three reconstructed (001) GaAs surfaces: (2×1) , $\beta(2 \times 4)$, and $\beta 2(2 \times 4)$.

We discuss first each of the reconstructed surface, and then provide a comparison between the three studied reconstructions.

1. Reconstruction (2×1)

We start the discussion of energetics of the Mn-pair adsorbed at the (001) GaAs surfaces with the case of the (2×1) surface reconstruction. We treat this case as a prototype and describe the methodology used to study Mn-pairs on other reconstructed surfaces. Two Mn-atoms can be substituted on Ga sites of the 4×4 lateral unit cell (see Fig. 2) in many ways as it is indicated in Fig. 3. We consider substitution of Mn-atoms into the second from top cationic (Ga) layer (the top layer consists of As atoms), i.e., for all considered configurations the Mn-pairs lie in the (001) crystallographic plane. First Mn-atom is substituted on Ga site indicated as "0", Mn(0). The possible position of the second Mn-atom is indicated by the crystallographic direction along which the pair can be placed $[k\bar{l}0]$ and the integer n ($n = 1, 2, 3, \dots$) that indexes possible positions of the second Mn along this direction. The configuration of the Mn(0)-Mn(n)-pair along the $[k\bar{l}0]$ direction will be indicated as $0 - n[k\bar{l}0]$ from now on. As it is seen in Fig. 3, there are three possible configurations of the Mn-pair along $[\bar{1}10]$ direction, but only two along $[110]$ and $[100]$ directions, and only one Mn-pair configuration along the $[310]$, $[\bar{5}10]$, $[3\bar{1}0]$, and $[\bar{2}10]$ directions. Because of the periodic boundary conditions imposed on the lateral supercell, some of the indicated possible Mn positions are

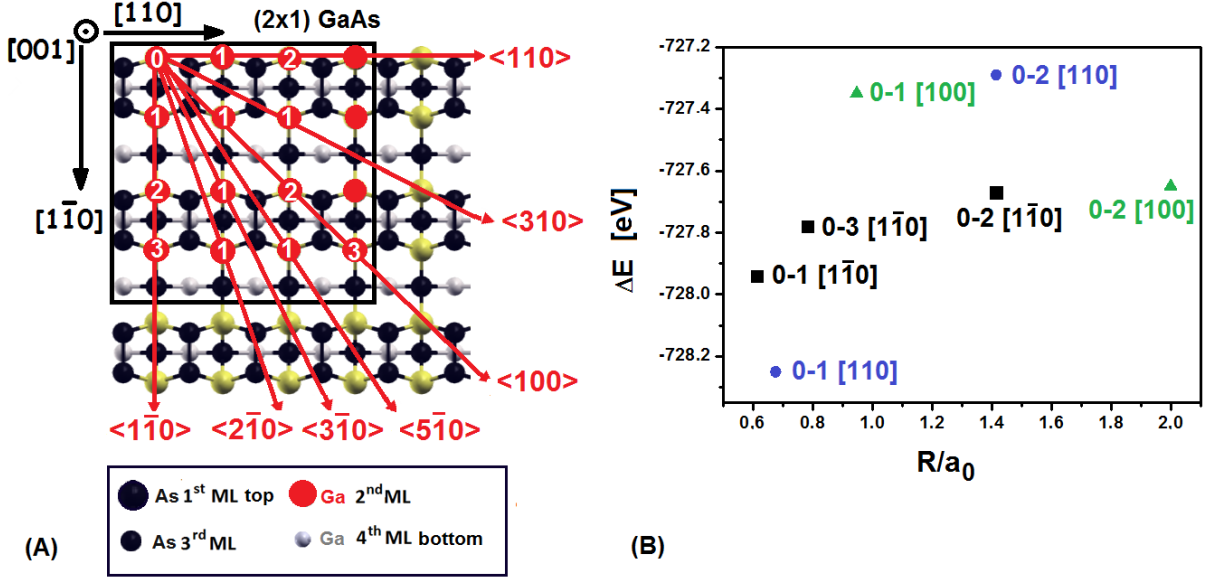


FIG. 3. (A) All non-equivalent positions of Mn-pair on the (2×1) reconstructed (001) surface. The two Mn-atoms, replacing Ga-atoms (red spheres), are marked 0 (first Mn-atom) and 1,2,3 (second Mn-atom), e.g. 0-3 $[1\bar{1}0]$ denotes that the Mn-pair is along $[1\bar{1}0]$ crystallographic direction, where Mn-atoms constituting the pair sit on 0 and 3 position as is depicted on panel (A). Note that the position 0-3 $[1\bar{1}0]$ is equivalent to position 1-2 $[1\bar{1}0]$ in a supercell, and so forth. All equivalent symmetry directions $\langle \dots \rangle$ have been chosen in direct cubic coordinates [...], in such a way that all Mn-pairs appear in (001) plane. Positions of the atoms in the uppermost monolayers are indicated by larger symbols. Positions of the As-atoms are denoted with big black dots. Small grey dots indicate the positions of the Ga-atoms. (B) The stability of systems with Mn-pair attached to the (2×1) reconstructed surface, measured as the LDA energy differences $\Delta E = E_{tot}^{slab, Mn-pair}(MS) - E_{tot}^{slab, pure}$ as the function of the Mn-Mn distance. For clarity, the energetically less stable configurations (defined in panel A) have been omitted here. The two most stable configurations are the ones with Mn-atoms being nearest neighbors along $[110]$ and $[1\bar{1}0]$ directions.

equivalent; specifically, the Mn(0)-Mn(3) pair is equivalent to the Mn(1)-Mn(2) pair. Altogether, one has 11 nonequivalent Mn-pairs in the 4×4 lateral unit cell of the (2×1) reconstructed surface: three with Mn-atoms being nearest neighbors on cationic sublattice (indicated as 0-1 $[1\bar{1}0]$, 0-1 $[110]$, 0-3 $[1\bar{1}0]$) with the Mn-Mn distances $R = 3.46\text{\AA}$, $R = 3.81\text{\AA}$, and $R = 4.41\text{\AA}$, respectively; a two with Mn-atoms being the second nearest neighbors (0-1 $[100]$, 0-1 $[2\bar{1}0]$), $R = 5.34\text{\AA}$ and $R = 5.95\text{\AA}$, respectively; two with Mn-atoms being the third nearest neighbors (0-2 $[1\bar{1}0]$, 0-2 $[110]$) with $R = 7.98\text{\AA}$; three with Mn-atoms being the fourth nearest neighbors (0-1 $[310]$, 0-1 $[3\bar{1}0]$, 0-1 $[5\bar{1}0]$), $R = 8.73\text{\AA}$, $R = 8.92\text{\AA}$, $R = 9.12\text{\AA}$, respectively; and one with Mn-atoms being the fifth nearest neighbors (0-2 $[100]$), $R = 11.29\text{\AA}$.

Having defined 11 configurations of the Mn-pairs placed onto the 4×4 lateral unit cell, we are now in the position to determine their relative energetic stability. We define the adsorption energy of Mn-pair in configuration 0- $n[kl0]$ employing the standard expression³²:

$$E_{ads}(0-n[kl0]) := E_{tot}^{slab, Mn-pair}(0-n[kl0]) - E_{tot}^{slab, pure} - (\mu_{Mn} - \mu_{Ga})N_{Mn}, \quad (1)$$

where N_{Mn} is the number of Mn-ions substituted on the Ga sites, and μ_{Mn} , μ_{Ga} are the chemical potentials of

Mn- and Ga-ions, respectively. However, since the number of substituted atoms in each considered configuration is identical, it is sufficient to consider only the total energy of the slab with 0- $n[kl0]$ Mn-pair normalized to the total energy of the pure slab:

$$\Delta E(0-n[kl0]) := E_{tot}^{slab, Mn-pair}(0-n[kl0]) - E_{tot}^{slab, pure}. \quad (2)$$

The values of this energy for some of the considered configurations 0- $n[kl0]$ versus the distance between the Mn-atoms are depicted in Fig. 3(B). It is clearly seen that the energetically most stable configuration of the Mn-pair on the (2×1) reconstructed (001) GaAs surface is the configuration with Mn-pair placed along the $[110]$ direction with Mn-atoms being the first neighbors on the cationic sublattice. It is so, even then, the distance between Mn-atoms in the 0-1 $[1\bar{1}0]$ configuration is smaller than in the 0-1 $[110]$ one. It demonstrates directional preference of accommodating Mn-pair on the (2×1) reconstructed surface, which results from the local environment of the Mn-pair. However, as expected and seen in Fig. 3(B), the configurations with Mn-atoms being further apart are generally energetically less favorable. It is strong indication of the tendency of Mn-atoms deposited on the surface to form pairs.

The energy difference between 0-1 $[110]$ and 0-1 $[1\bar{1}0]$

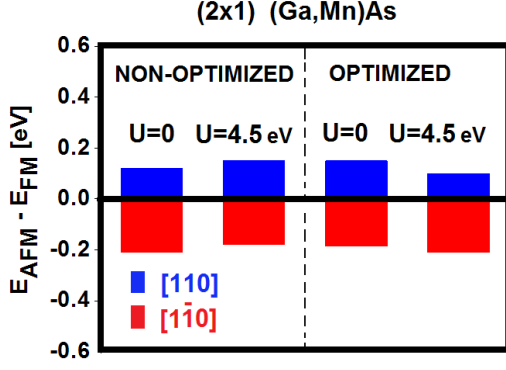


FIG. 4. The energy difference between AFM and FM Mn-spin alignment $E_{AFM} - E_{FM}$ in eV/supercell, for the nearest neighbor 0-1 Mn-pair along the $[1\bar{1}0]$ (red) and $[110]$ (blue) directions at (2×1) reconstructed surface, as calculated within standard LSD (indicated by $U=0$) and L(S)DA+ U (indicated by used value $U=4.5$ eV) methods. For Mn-pair along $[1\bar{1}0]$ direction, the magnetic ground state is antiferromagnetic (AFM), whereas for $[110]$ direction, it is ferromagnetic one (FM). It is seen that optimization of atomic positions does not change magnetic state of the system.

configurations of Mn-pair is 0.4 eV per supercell with 288 atoms. It is obvious that the local changes of the geometry contribute considerably to the relative stability of these two configurations. It is worth to point out now that when we place Mn-pair along $[110]$ crystallographic direction, the symmetry is lowered to C_v in comparison to pure (2×1) reconstructed (001) GaAs surface (where it is C_{2v}), whereas Mn-pair placed along the $[1\bar{1}0]$ direction doesn't change the symmetry of the layer. As a consequence, we have noticed stronger relaxation of the atoms around the Mn-pair along $[110]$ direction, than for the Mn-pair along the $[1\bar{1}0]$ direction.

All the results concerning relative stability of Mn-pairs described above have been obtained employing standard nonmagnetic calculations with LDA exchange-correlation functional. It is apparent that the change of the energy owing to the local rearrangement of atoms in the neighborhood of Mn-pair is of the order of the magnetic energy of the Mn-pair. Therefore, we included the magnetic interaction into our study employing the standard local spin density approximation (L(S)DA) and L(S)DA+ U calculations. Employing these two methods, we consider parallel (ferromagnetic - FM) and antiparallel (antiferromagnetic - AFM) ordering of localized magnetic moments of Mn-atoms constituting the Mn-pair on the nearest neighbor cationic positions along $[110]$ and $[1\bar{1}0]$ directions. We use the standard value of $U = 4.5$ eV parameter for Mn-atom that has been routinely used in many calculations involving Mn²⁰⁻²². For non-optimized atomic position around the Mn-pair, the AFM ordering of Mn magnetic moments in Mn-pair is more favorable than FM one for $[1\bar{1}0]$ direction, whereas for Mn-pair along the $[110]$ direction the relation is reversed. The full relaxation of the slab does not change this picture

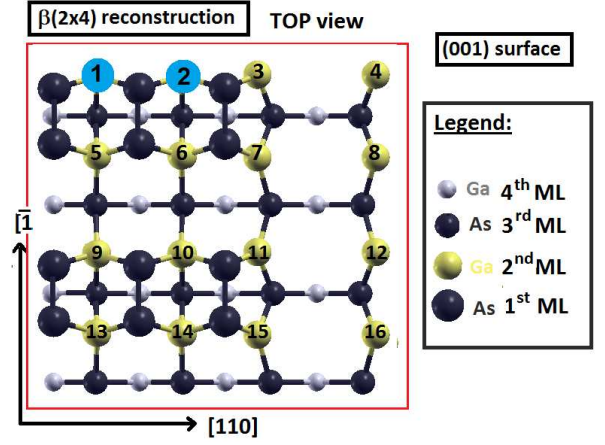


FIG. 5. Positions of Mn-pairs at the $\beta(2 \times 4)$ reconstructed surface. The energetically most favorable position is for Mn-pair indicated as 1 & 2 along $[110]$ direction with FM ordering of spins. For emphasis, this pair is indicated by the blue color. This is true for both L(S)DA and L(S)DA+ U calculations. All other cationic positions, where Mn-atoms can be substituted are indicated by yellow color and numbered 3-16. Note that 5 & 6 positions of Mn-atoms are equivalent to 1 & 2 and lead to the same energy. Positions of the As-atoms are indicated with big and small black dots for the highest and deeper As-layers, respectively.

as it is illustrated in Fig. 4. Qualitatively the same picture is obtained for L(S)DA and L(S)DA+ U functionals. For the L(S)DA+ U method, the energies defined in equation 2 are as follows $\Delta E(0 - 1[110]; FM) = -735.90$ eV; $\Delta E(0 - 1[110]; AFM) = -735.81$ eV; $\Delta E(0 - 1[1\bar{1}0]; AFM) = -735.54$; $\Delta E(0 - 1[1\bar{1}0]; FM) = -735.34$ eV. Therefore, the most stable configuration of the Mn-pair adsorbed at the (2×1) reconstructed (001) GaAs surface is $0 - 1[110]$ with parallel magnetic moments of two Mn-atoms.

The discussion for the (2×1) reconstructed surface sheds light on the energetics of the Mn-pair adsorption. It clearly demonstrates the interplay between the magnetic interactions of the Mn-atoms and atomic relaxations around them. Further, we follow the discussion for Mn-pairs adsorbed to the $\beta(2 \times 4)$ and $\beta_2(2 \times 4)$ reconstructed surfaces. However, in the light of results obtained for (2×1) reconstructed surface, we focus the discussion on Mn-pairs placed along $[110]$ and $[1\bar{1}0]$ crystallographic directions.

2. Reconstruction $\beta(2 \times 4)$

We start the discussion with a survey of possible placements of the Mn-pairs on the $\beta(2 \times 4)$ (001) GaAs surface (see Fig. 5). In the chosen supercell of C_{2v} symmetry, the $[110]$ and $[1\bar{1}0]$ directions are non-equivalent. Along each of these directions, we can place the nearest neighbor Mn-pair on four equivalent ways on the cationic sublattice. They are, 1 & 2, 5 & 6, 9 & 10, 13 & 14, for $[110]$,

TABLE I. The stability of the systems with the adsorbed Mn-pairs at the $\beta(2 \times 4)$ reconstructed (001) GaAs surface measured by the energy $\Delta E = E_{tot}^{slab, Mn}(MS) - E_{tot}^{slab, pure}$, given in eV per supercell. The Mn-pair positions are explained in Fig. 5. $E_{tot}^{slab, pure} = -39813.12$ eV per supercell with 284 atoms. The parallel and antiparallel spin alignment of the Mn-pair is indicated by FM and AFM, respectively. The results are obtained employing standard L(S)DA and L(S)DA+U ($U = 4.5$ eV) approaches.

$\beta(2 \times 4)$	$\Delta E_{L(S)DA}$ [eV/cell]		$\Delta E_{L(S)DA+U}$ [eV/cell]	
Mn-pair position	FM	AFM	FM	AFM
[110] 1 & 2	-737.743	-737.448	-743.792	-743.555
[110] 2 & 3	-737.582	-737.456	-743.765	-743.666
[110] 3 & 4	-737.561	-737.413	-743.756	-743.636
$[\bar{1}\bar{1}0]$ 6 & 10	-737.415	-737.455	-743.521	-743.582
$[\bar{1}\bar{1}0]$ 7 & 11	-737.095	-737.053	-743.443	-743.430
$[\bar{1}\bar{1}0]$ 10 & 14	-737.539	-737.557	-743.627	-743.623
$[\bar{1}\bar{1}0]$ 11 & 15	-737.195	-737.318	-743.605	-743.697

and 1 & 5, 2 & 6, 9 & 13, 10 & 14 for $[\bar{1}\bar{1}0]$ directions, respectively.

However, along the $[110]$ and $[\bar{1}\bar{1}0]$ directions we can place Mn nearest neighbor pairs also in non-equivalent positions, such as 1 & 2, 2 & 3, 3 & 4, along $[110]$, and 6 & 10, 7 & 11, 10 & 14, 11 & 15 along $[\bar{1}\bar{1}0]$. The difference in energy for the nearest neighbor (NN) configurations mostly stems from the fact that the surroundings of Mn-pairs are different, but also to a lesser extent, that the distance (after relaxation of atoms) between the Mn-atoms constituting the pair also has been changed.

From Fig. 5, one can also deduce the positions of the Mn-pairs with longer than nearest neighbor distances between Mn-atoms. We have performed calculations for all non-equivalent positions of the Mn-pairs. It turns out that the pairs with Mn-atoms being the nearest neighbors are energetically preferable in comparison to the configurations with larger distances between the Mn-atoms.

However, the relative energy differences among this class of configurations are dependent on the alignment of magnetic moments of the Mn-atoms (FM or AFM). This is illustrated in Table I, where the difference of the total energies of slab with Mn-pair and the pure slab (i.e., without Mn-pair) are given for the L(S)DA and L(S)DA+U method.

Note that the total energy of the pure slab can be considered as a reference energy. This energy is identical for the L(S)DA and L(S)DA+U case, since for the atoms in the pure slab (As, Ga, H) the Hubbard term U has been always taken as zero.

The energies of all non-equivalent Mn-pair arrangements (with Mn-atoms being the nearest neighbors) are presented in Table I.

Among the NN Mn-pairs placed along $[110]$ direction,

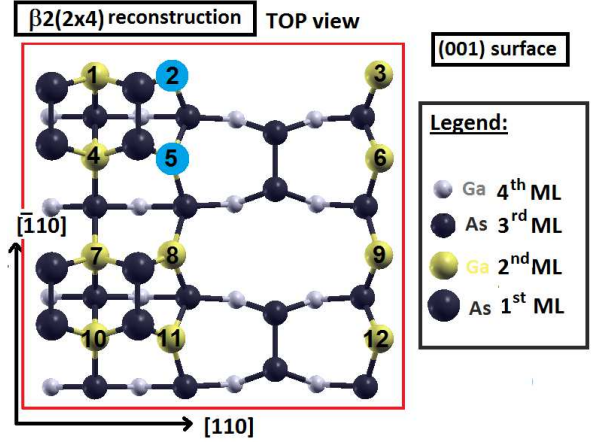


FIG. 6. Positions of Mn-pairs at the $\beta(2 \times 4)$ reconstructed surface. According to L(S)DA+U approach, the energetically most favorable configuration is the one with Mn-pair (indicated as 2 & 5) along $[\bar{1}\bar{1}0]$ direction with AFM ordering of spins. This configuration has been indicated by blue color. All other possible position of Mn-atoms on cationic sublattice are indicated by yellow color and numbered 3-12. Positions of the As-atoms are indicated with big and small black dots for the highest and deeper As-layers, respectively.

the lowest total energy is for FM Mn-spin arrangements and the Mn-pairs 1 & 2 (see Fig. 5, where this pair is indicated in blue). This is true for both L(S)DA and L(S)DA+U approaches. Among all NN Mn-pairs placed along $[\bar{1}\bar{1}0]$ direction, the lowest total energy is for the AFM spin configuration for the Mn-pair 10 & 14 in L(S)DA approach (see Fig. 5) and for the Mn-pair 11 & 15 when L(S)DA+U approach is employed. Generally, the L(S)DA and L(S)DA+U approaches lead to identical trends concerning the interplay between magnetic ordering and local environment of Mn-pairs. For all Mn-pairs along $[110]$ direction, the FM alignment of Mn-spins is favorable over the AFM one. For Mn-pairs along $[\bar{1}\bar{1}0]$ directions, generally the AFM spin alignment leads to lower energies than the FM one, however it is not the case for Mn-pair numbered 7 & 11.

3. Reconstruction $\beta(2 \times 4)$

We discuss now structural and energetic properties of the Mn-pairs on cationic sublattice and placed onto the $\beta(2 \times 4)$ reconstructed (001) surface. As in the $\beta(2 \times 4)$ case, we start the discussion with a survey of possible placements of the Mn-pairs onto the $\beta(2 \times 4)$ (001) GaAs surface (see Fig. 6). In the chosen symmetry of the supercell, the $[110]$ and $[\bar{1}\bar{1}0]$ directions are non-equivalent. Along the $[110]$ crystallographic direction, one can place the nearest neighbor Mn-pair in eight equivalent ways on the cationic sublattice, 1 & 2, 4 & 5, 7 & 8, 10 & 11, 1 & 3, 4 & 6, 7 & 9, and 10 & 12, which results in one class of non-equivalent positions represented by

TABLE II. The stability of the systems with the adsorbed Mn-pairs at the $\beta 2(2 \times 4)$ reconstructed (001) GaAs surface measured by the energy $\Delta E = E_{tot}^{slab,Mn}(MS) - E_{tot}^{slab,pure}$, given in eV per supercell. The Mn-pair positions are explained in Fig. 6. $E_{tot}^{slab,pure} = -38570.17$ eV per supercell with 274 atoms. The parallel and antiparallel spin alignment of the Mn-pair is indicated by FM and AFM, respectively. The results are obtained employing standard L(S)DA and L(S)DA+U ($U = 4.5$ eV) approaches.

$\beta 2(2 \times 4)$	$\Delta E_{L(S)DA}$ [eV/cell]		$\Delta E_{L(S)DA+U}$ [eV/cell]	
Mn-pair position	FM	AFM	FM	AFM
[110] (1 & 2)	-733.684	-733.483	-739.621	-739.465
[1-10] (1 & 4)	-733.825	-733.852	-739.601	-739.604
[1-10] (2 & 5)	-733.531	-733.571	-739.610	-739.693
[1-10] (4 & 7)	-733.855	-733.892	-739.614	-739.552
[1-10] (5 & 8)	-733.483	-733.386	-739.530	-739.459

1 & 2. Along the $[1\bar{1}0]$ direction, there are four classes of non-equivalent positions of the Mn-pair. They were chosen to be 1 & 4, 2 & 5, 4 & 7, and 5 & 8. Note that 1 & 4 and 7 & 10 or 5 & 8 and 6 & 9 are equivalent. Our results show that the pairs with Mn-atoms being the nearest neighbors are energetically preferable in comparison to the configurations with larger distances between the Mn-atoms. In table II, we present the relative energy differences among all nearest neighbor classes of Mn-dimer configurations for FM and AFM alignments of magnetic moments of the Mn-pair.

The analysis of energies presented in table II reveals following picture. For Mn-pair along [110] direction, the FM alignment of spins is energetically more favorable than the AFM one (in both L(S)DA and L(S)DA+U approaches), as it was observed for the $\beta(2 \times 4)$ reconstruction. However this configuration (in contrast to the case of the $\beta(2 \times 4)$ reconstruction) is not the most stable one. The most stable configurations are observed for Mn-pairs along $[1\bar{1}0]$ directions. According to the standard L(S)DA the most stable configuration is the one with Mn-atoms 4 & 7 along $[1\bar{1}0]$ with AFM Mn-spins alignment, whereas the L(S)DA+U predicts the 2 & 5 pair (indicated by blue color in Fig. 6) with AFM spin alignment to be the most energetically favorable. However, one has to have in mind that the differences in energies of different configurations are extremely tiny.

4. Comparison between different reconstructions

In this section, we make an attempt to generalize our theoretical studies presented in the previous sections and get physical understanding of the structural and energetic properties of (001) GaAs surfaces decorated with Mn-pairs.

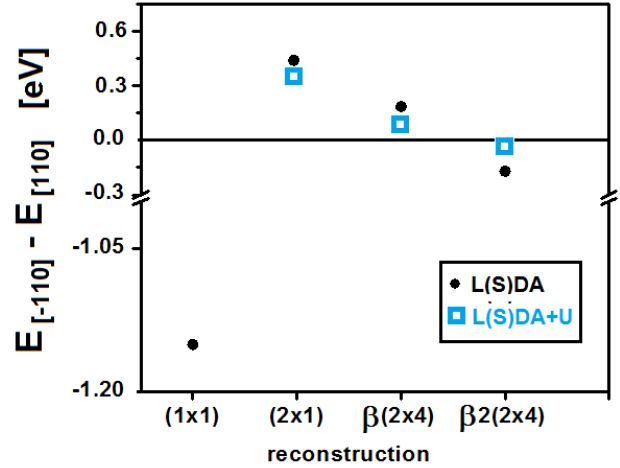


FIG. 7. Comparison of the most stable configurations of the Mn-pairs at surfaces with various reconstructions. The energy difference between the most stable NN configuration at $[1\bar{1}0]$ and $[110]$ crystallographic directions, as obtained within the L(S)DA and L(S)DA+U schemes.

Our results show that the energy of the system strongly depends on the position, orientation, the distance between the Mn-atoms, and relative alignment of Mn-spins. The Mn-pairs prefer to occupy the nearest neighbor positions (NN) independently on the reconstruction type at the surface. In other words they prefer to form dimers at the surface.

It turns out that for Mn-dimers there are two crystallographic orientations leading to the energetically most stable configurations, namely the $[110]$ and $[1\bar{1}0]$ crystallographic directions. The energy differences between the most stable configurations along the $[1\bar{1}0]$ and $[110]$ directions (as obtained within the L(S)DA and L(S)DA+U schemes) are summarized for all considered surface reconstructions in Fig. 7. One can see that the energetically preferential orientation of the Mn-dimer depends on the surface reconstructions. In other words, it is plausible that during the growth process the Mn-ions would accommodate positions along the energetically preferential directions. The very recent measurements have shown that there exist magnetic inhomogeneities on sub-millimeter length scales in (Ga,Mn)As samples³³, which can be assigned to anisotropic picture of Mn distribution. Moreover, our results have touched very important issue of the origin of the uniaxial magnetic anisotropy in (Ga,Mn)As samples. Recently, the authors have shown⁶ that the preferential distribution of Mn-atoms at the surface is the physical origin of the symmetry breaking of the bulk GaAs crystal and consequently of the bulk uniaxial in-plane and out-of-plane magnetic anisotropies. Our results suggest that by changing the growth conditions (the reconstructions on the surface depend on it) one can design the direction of the magnetic easy axis in (Ga,Mn)As samples.

Furthermore, our results give also some hints how to

change the preferential direction of the Mn-pairs at the surface, simply by changing the surface reconstructions through the choice of suitable growth conditions.

Finally we compare the stability of the pure surface with the stability of the just calculated surfaces with the incorporated Mn-dimers, which could mimic the surfaces of (Ga,Mn)As. Stability of the structure can be determined by the standard thermodynamics, and have been well established for systems in equilibrium³⁴. The most stable surface structure is determined by the minimum of the surface free energy γ , which is given by the equation below:

$$\gamma = \frac{1}{A}(E_{slab} - nE_{bulk} - \sum_i \mu_i N_i), \quad (3)$$

where A is the surface area of the slab within the supercell, E_{slab} denotes the total energy of the supercell, n is the number of bulk unit cells contained in the slab cell, and having energy E_{bulk} , and μ_i is the chemical potential of species i . In order to plot the surface free energy versus the thermodynamically allowed range of chemical potential, the surface free energy can be re-expressed as a function of the differences in the chemical potentials of the atomic As and As-bulk, $\Delta\mu = \mu_{As} - \mu_{As}^{bulk}$, by using the thermal equilibrium conditions³⁴

$$\gamma = \frac{1}{A}(E_{slab} - nE_{GaAs}^{bulk} - N_{Ga}E_{GaAs}^{bulk} - N_{Mn}E_{MnAs}^{bulk} - (\mu_{As} - \mu_{As}^{bulk})\Delta N - \mu_{As}^{bulk}\Delta N), \quad (4)$$

where the stoichiometry parameter is defined as $\Delta N = (N_{As} - N_{Ga} - N_{Mn})$, and E_x^{bulk} is the cohesive energy of either the MnAs or GaAs systems when $T \rightarrow 0K$. Our calculated heat of formation for MnAs is $\Delta H_f^{MnAs} = -0.52$ eV, and for GaAs is $\Delta H_f^{GaAs} = -0.73$ eV per unit cell with 2 atoms for both systems.

The surface energies for the systems studied in this paper are presented in Fig. 8 for L(S)DA approach. There, one can see that the pure $\beta 2(2 \times 4)$ reconstructed (001) GaAs surface is the most stable one for the whole range of chemical potential. This is a consequence of the dimerization of the atoms at the surface, which reduces the numbers of dangling bonds and creates the sp^2 like bonds. The difference between the $\beta(2 \times 4)$ and $\beta 2(2 \times 4)$ surface energies is 4 meV/ \AA^2 , which is the same order of magnitude as reported previously in literature, where this difference was reported to lie in the range 2–3 meV/ \AA^2 ^{27,35}. Moreover, one can see that all the reconstructions considered in Fig. 8 become more stable at the As-rich limit, i.e., $\mu_{As} - \mu_{As}^{bulk}$ approaching zero. The $\beta 2(2 \times 4)$ reconstructed surface with Mn-pair along $[1\bar{1}0]$ direction is found to be energetically the most favorable of all Mn-reconstructed surfaces considered in this paper, however, only a little bit lower (3 meV per \AA^2), than the surface with Mn-pair along the $[110]$ direction.

Generally, incorporation of the Mn-dimer into substitutional position at given reconstructed surface destabilizes this surface by 55 meV/ \AA^2 - 59 meV/ \AA^2 .

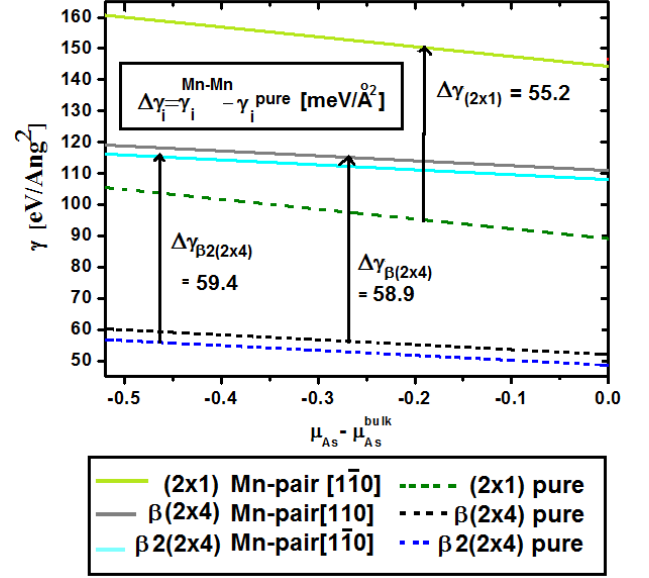


FIG. 8. Surface free energy diagrams for pure (001) GaAs, As-terminated surface reconstructions: (2×1) , $\beta(2 \times 4)$, $\beta 2(2 \times 4)$ (denoted by the dashed lines), and for the most energetically preferable Mn-dimer substitutional incorporations onto these reconstructed surfaces (denoted by the straight lines) as predicted in this paper. Thermodynamically allowed range of the difference of chemical potentials of As-atom and As-bulk is between -0.52 eV (Ga-rich conditions) and 0.00 eV (As-rich conditions). The arrows indicate the change in the surface free energy $\Delta\gamma_i$ owing to the incorporation of Mn-dimer. One can see that the Mn-dimer incorporation destabilizes the given pure reconstructed surface by 55–59 meV/ \AA^2 .

B. Magnetic and Electronic Properties

In this section, we focus on the strength of the magnetic interaction of Mn-pairs at studied surfaces. Then we examine the electronic structure and spin magnetic moments.

In order to show how the strength of the magnetic interaction of the Mn-ions changes with the Mn-Mn distance, we plot the absolute value of energy difference between AFM and FM alignments of the magnetic moments of Mn-atoms as a function of their separation (see Fig. 9). We assume collinear magnetic configurations of Mn-ions in which magnetic moments are either parallel or antiparallel. We do not include spin-orbit interaction, because it has been reported recently, that the SOI have a small influence on exchange coupling J (few meV)¹².

Since the exchange interaction is a crucial quantity in the field of DMS, we start our discussion comparing our results with the other theoretical predictions taken from literature^{11,12,22,33} (see Fig. 9), for both bulk and surface calculations obtained within different methods and different concentration of Mn-ions. We would like to stress that the two older surface calculations^{11,12} dealt with non-polar $[110]$ GaAs surface that exhibits pronounced

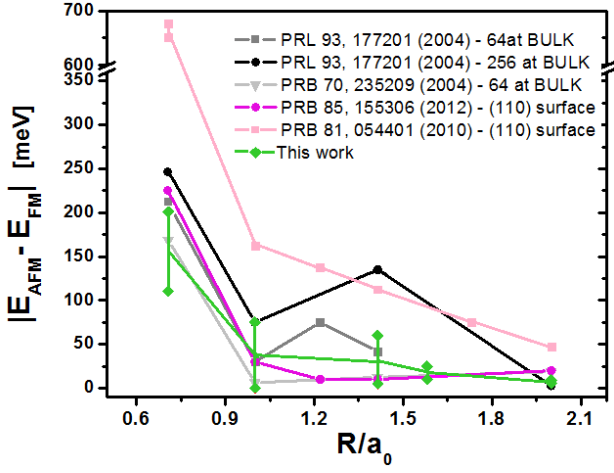


FIG. 9. The absolute value of the total energy difference between ferromagnetic and antiferromagnetic alignments of two Mn-spins as a function of Mn-Mn separation (in lattice constant units a_0) for the surface and bulk calculations. The green line presents the result of this work for the surface reconstruction (2×1), and the green vertical lines indicate the obtained range of the magnetic energies for various Mn-pair configurations for given separation between the Mn-ions. The internal panel shows the sources of data.

differences in comparison to the surfaces studies here.

The general trends of the exchange energy of Mn-pair at surfaces and in the bulk are similar, generally exhibiting a decay of the magnetic interaction with increasing distance between the magnetic ions.

The main difference between our and previously reported results is that we obtain anisotropic character of the magnetic energy without taking into account spin-orbit interaction SOI. Only Strandberg *et al.*¹¹, who took into account the SOI, reported the difference of around 13 meV between two non-equivalent positions of the NN pairs³⁶. In our calculations the changes are around hundredths of meV. This is the result of taking into account reconstructed surfaces, which provide many possibilities of placement of two Mn-ions at given distance between them. Below we demonstrate the detailed studies of the exchange coupling constants.

1. Effective exchange coupling

We have analyzed the effective exchange constant J for the all non-equivalent NN distance between the Mn-ions at reconstructed (001) GaAs surfaces: (2×1) , $\beta(2 \times 4)$, and $\beta 2(2 \times 4)$ (see table III), according to the formula: $J = (E_{AFM} - E_{FM}) \cdot (2 \cdot (5/2)^2)$. Here we assume the spin magnetic moments of Mn-atoms to be $5/2$.

Our results clearly demonstrate that the Mn-dimer along $[110]$ crystallographic direction exhibits ferromagnetic alignment of spins, i.e., positive values of the exchange coupling J (see table III), with magnetization vectors on each Mn-atom being oriented along the $[001]$ di-

TABLE III. The exchange coupling J given in meV for the nearest neighbor Mn-pairs for various considered reconstructed surfaces. The numbers in brackets delimit the obtained range of the exchange coupling. The results are obtained employing standard L(S)DA and L(S)DA+U (for $U = 4.5$ eV) approaches.

J [eV]	(2×1)	$\beta(2 \times 4)$	$\beta 2(2 \times 4)$
Mn-Mn pair along $[110]$			
L(S)DA	+12	[+12, +24]	+16
L(S)DA+U	+7	[+8, +19]	+13
Mn-Mn pair along $[1\bar{1}0]$			
L(S)DA	[-16, -13]	[-10, +4]	[-3, +8]
L(S)DA+U	[-18, -16]	[-7, +1]	[-7, +6]

rection and of magnitude equal to $4.7 \mu_B$, independently of the type of reconstructed surface. For the dimer along $[1\bar{1}0]$ crystallographic direction, the anti-ferromagnetic alignment of the spins is most likely to appear (mostly negative values of the exchange coupling J , see table III). In other words, the mechanism of the magnetic ordering has the anisotropic character, namely it depends on the Mn-pair orientation. This rises a question whether it would be possible (e.g., by the STM method) to incorporate on purpose the magnetic atoms along a given direction at the surface. Then one could obtain on purpose magnetic or non-magnetic material. One can see that the value of the exchange constant for a given orientation of Mn-dimer depends on the type of surface reconstruction, indicating that the exchange constant depends sensitively on the lattice arrangement of the atoms.

Now we compare our result with the exchange coupling for the dimer reported so far in the literature. Those reports show that the effective J for the dimer is highly sensitive to doping levels and increases with decreasing Mn concentration^{22,33,37,38}. The order of magnitude of the exchange coupling calculated in our studies is the same as previously reported for the surface and bulk results. However, the bulk calculations always predict the ferromagnetic ordering of the Mn-spins.

To our knowledge, previous surface calculations considered only the unreconstructed (110) non-polar GaAs surface. The authors of Ref.¹² obtained, within the GGA approximation of DFT, a J value equal to 17.9 meV³⁹ for the nearest neighbor configuration. Strandberg *et al.*¹¹ obtained positive values of J for two different directions of Mn-dimer at the (110) surface, 54 meV and 53 meV, for the very low Mn concentration of $x = 0.0006$. They used the kinetic tight binding model. Due to the restrictions of the model they did not take into account relaxations of the atoms at the surface. This can significantly influence the results. Therefore, we believe that our studies provide reliable quantitative theoretical predictions and shed light on physical mechanisms leading to magnetic structure of Mn-pairs on the (001) GaAs surfaces. Further, we corroborate that the ordering mechanism of Mn-spins

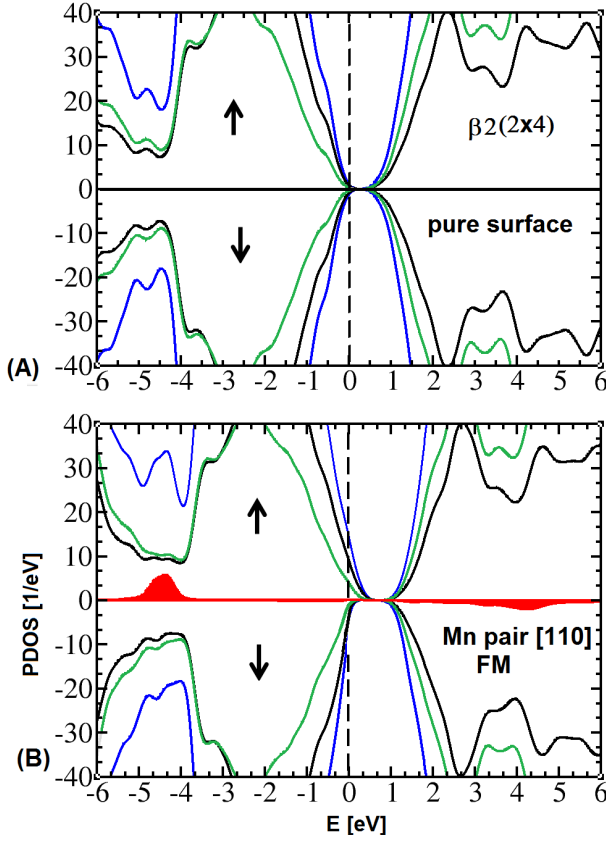


FIG. 10. Projected DOS calculated within L(S)DA+U method for: (A) pure $\beta 2(2 \times 4)$, and (B) the Mn-dimer substituted onto cationic sublattice along [110] crystallographic direction at the $\beta 2(2 \times 4)$ surface. The pure $\beta 2(2 \times 4)$ surface is semiconducting, whereas substituted Mn-ions introduce extra states above the Fermi level within the valence band. The vertical dashed line denotes the position of the Fermi level. The solid blue, black, and green lines correspond respectively to total density of all states in a system, total density of As-states, and total density of Ga-states. The red area is the contribution from Mn d states. The positive values of PDOS represent spin-up channel, negative spin-down one.

is governed by the local environment of Mn-atoms.

2. Electronic structure and spin magnetic moments

Let us discuss now the changes of electronic structure caused by adsorption of Mn-dimer onto the reconstructed (001) GaAs.

The pure (2×1) surface is metallic and the surface states are placed in the bandgap of the bulk, whereas the pure β -surfaces are semiconducting (see Fig. 10(A)) and do not introduce the surface states into the bulk's gap. When the two Ga-ions are substituted by the Mn-ions, the extra electronic states appear just above the Fermi level (see Fig. 10(B)). These empty states which are above the Fermi level and belong to the valence band can be identified with the hole states. As hole states we consider

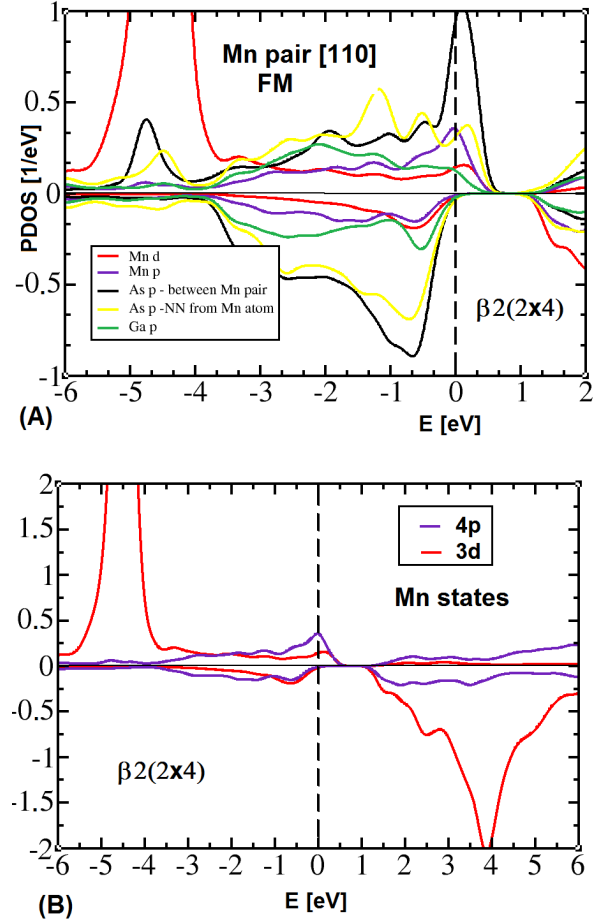


FIG. 11. PDOS as obtained from the L(S)DA+U calculations for the Mn-pair at the reconstructed $\beta 2(2 \times 4)$ surface. (A) Contribution of the surrounding atoms of the Mn-dimer along the [110] crystallographic direction, and (B) the comparison between the Mn p and d states.

unoccupied states with energies between Fermi energy (lying in the valence band)⁴⁰ and top of the valence band, as it was previously considered for a bulk system^{41,42}. The hole states have mostly p character (see Fig. 11(A)).

The greatest contribution to the holes comes from the arsenic atoms, which are the nearest neighbors of the Mn-pair and reside along the [110] crystallographic direction (see Fig. 11(A)). Moreover, the $3d$ states are mainly localized around 4.5 eV below the Fermi level (see Fig. 11(B)). Therefore, the Mn p states hybridize with the surrounding stronger than the $3d$ states. There is only small admixture of the Mn d -states with the hole states.

Now let us discuss the spatial distribution of the hole, in order to visualize its character.

The hole occupation N_h is defined here as the integral over energy of the density of states from the Fermi energy to the top of the valence band. Note that the same procedure was previously adopted in Refs.⁴¹ and⁴² for the bulk system. One can also consider integrated den-

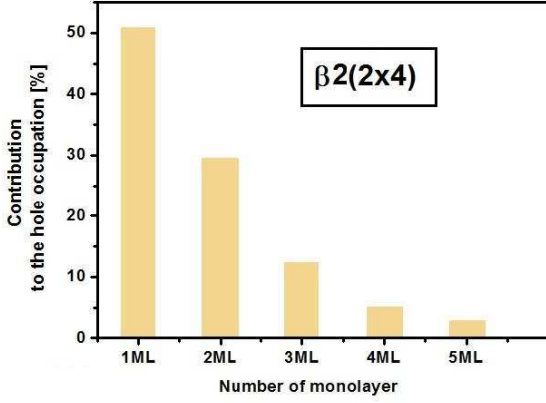


FIG. 12. Contribution [in %] to the hole occupation coming from various layers of the slab representing $\beta 2(2 \times 4)$ reconstructed (001) GaAs surface with adsorbed Mn-dimer along the [110] direction. 1ML indicates the top layer of As-atoms, 2ML indicates the Ga-atoms layer just below the top As-layer. The Mn-dimer is placed in this layer. 3ML & 5 ML one As-layers, 4ML is Ga-layer. The higher the number the deeper position of the layer relative to the top one (1ML).

sity of states $N_{h,layer}$ coming from the projected DOS for various slab layers. The analysis of the contribution of the various layers to the total hole density (N_h) defined above is presented in Fig. 12 in the case of the $\beta 2(2 \times 4)$ reconstructed surface.

It is clearly seen that the contribution to the total hole occupancy decreases quickly with the depths of the layer, and the highest two layers (indicated as the 1ML & 2ML in Fig. 12) contribute 80% of the hole density. This result sheds light on the degree of hole delocalization. We would like to emphasize that in our calculations no impurity band related to surface acceptor has been observed. This clearly corresponds to the Zener type (or RKKY one)⁴³ of magnetic coupling between Mn-ions, and the picture of surface, ligand-ion, $p-d$ interaction is the adequate one.

The electronic structure of the $\beta 2(2 \times 4)$ reconstructed (001) GaAs surfaces with the Mn-dimer with FM ordering of spins placed along [110] direction exhibits essentially all features of the case of $\beta 2(2 \times 4)$ reconstructed surface discussed above. It is illustrated in Fig. 13(A). For comparison, we plot also density of states for the Mn-dimer along $[1\bar{1}0]$ direction of three types of the reconstructed surfaces in Fig. 13(B).

Now let us focus on distribution of magnetic moments in the surrounding of the Mn-pair by using a Mulliken analysis⁴⁴. Our results clearly show that the local magnetic moments of Mn-ions polarize their surrounding always in such a way, that the nearest neighbor As-atoms acquire the magnetic moments anti-ferromagnetically aligned to the Mn-spins, which is schematically illustrated in Fig. 14 for the case of (2×1) reconstructed surface. For Mn-pair along [110] direction (i.e., with FM ordering of spins), the values of magnetic moments on

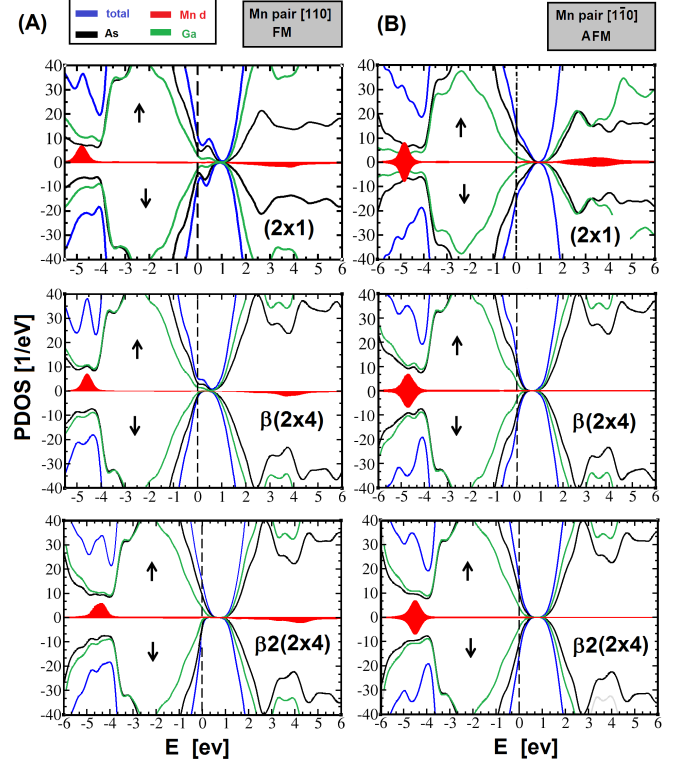


FIG. 13. PDOS calculated within L(S)DA+U method for the three reconstructed surfaces of GaAs with Mn-dimer along two different orientations: [110] (left side of the picture) and $[1\bar{1}0]$ (right side of the picture). Spin alignments for Mn-dimers are FM and AFM, for direction [110] and $[1\bar{1}0]$, respectively. The vertical dashed line denotes the position of the Fermi level. The solid blue, black, and green lines correspond respectively to total density of all states in a system, total density of As-states, and total density of Ga-states. The red area indicates the contribution from Mn d states.

As-atoms surrounding Mn ones are listed for three considered surface reconstructions in Table IV.

One can see that the induced magnetic moments are comparable and do not depend on the type of reconstructed surfaces. They decrease rapidly with the increasing distance to the Mn-pair. Only the nearest neighbors of the Mn-pair have (i.e., these depicted in Fig. 14) noticeable induced spin polarization. For the second neighbors, the induced magnetic moments are smaller than $0.01 \mu_B$, and for the third neighbors, the magnetic moments are nearly equal to zero. The same picture emerges from both L(S)DA and L(S)DA+U calculations. In the bulk system, the magnetic moment on the first, second, and third Mn neighbor extends to $0.11 \mu_B$, $0.015 \mu_B$, and $0.015 \mu_B$, respectively (according to the L(S)DA+U results from²²). This comparison between the bulk and the surface shows that the induced magnetic moments are more localized at the surface than in the bulk. In addition, the induced magnetic moments on the atoms are always larger at the surface than at the monolayer closer to the bulk site. In the case of AFM

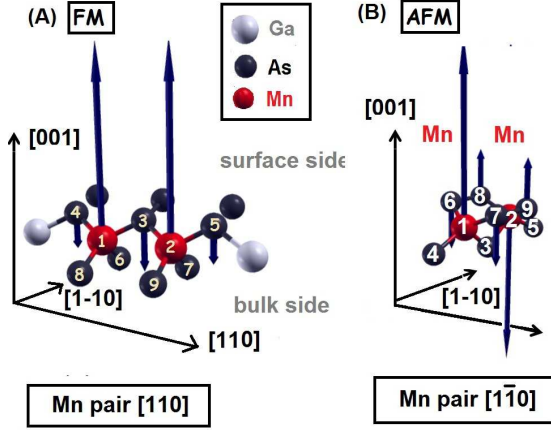


FIG. 14. Distribution of magnetic moments on As-atoms surrounding the Mn-dimer placed along $[110]$ (A) and $[1\bar{1}0]$ (B) crystallographic directions at the (2×1) reconstructed (001) GaAs surface. The blue arrows indicate the magnetic moments of Mn-atoms with FM (A) and AFM (B) alignments. The lengths of the magnetic vectors on As-sites are exaggerated for clarity of the presentation.

TABLE IV. The spin magnetic polarization (in μ_B per atom) of the As-atoms surrounding Mn-ions for the FM arrangement of Mn-pair at $[110]$ direction for various reconstructed surfaces, as calculated by using a Mulliken analysis⁴⁴. The As-atoms are numbered according to the Fig. 14.

atom	Surface reconstruction		
	(2×1)	$\beta(2 \times 4)$	$\beta 2(2 \times 4)$
As3	-0.74	-0.75	-0.79
As4	-0.2	-0.17	-0.2
As5	-0.2	-0.17	—
As9 = As7	-0.12	-0.10	-0.17
As8 = As6	-0.12	-0.10	-0.09

alignment of Mn-spins, the As-atom positioned between the Mn-dimer is not spin polarized. Other As neighbors of Mn-atoms have similar absolute values of spin polarization as in the FM case.

IV. CONCLUSIONS

We have studied the stability, morphology, and electronic structure of Mn-pairs substituted onto Ga sublattice at different As-terminated reconstructed (001) GaAs surfaces. We have demonstrated that the energy of the system depends on the position, orientation, and the distance between the Mn-atoms. The Mn-pairs with Mn-atoms being the nearest neighbors (i.e., constituting Mn-dimer) are energetically the most favorable, in-

dependently on the surface reconstruction pattern. This causes that there are only two crystallographic directions, namely $[110]$ and $[1\bar{1}0]$ relevant for adsorption of Mn-dimer. For (2×1) and $\beta(2 \times 4)$ reconstruction patterns, the Mn-dimer placed along $[110]$ direction is more stable than Mn-dimer placed along $[1\bar{1}0]$ direction. On the contrary, for (1×1) and $\beta 2(2 \times 4)$ reconstructions, the energetically stable configuration of the system requires Mn-dimer along the $[1\bar{1}0]$ direction. Our results point out to a possibility of affecting the magnetic anisotropy of the (Ga,Mn)As layer³ by forcing an alternative reconstruction of the semiconductor surface, during the growth, by choosing appropriate growth conditions — namely the vapor pressure, temperature or surface composition^{45,46}. Moreover, we have demonstrated that the mechanism of the magnetic ordering depends on the Mn-pair orientation. Generally, the Mn-dimer along $[110]$ crystallographic direction exhibits ferromagnetic alignment of the spins, whereas the Mn-dimer along $[1\bar{1}0]$ crystallographic direction prefers to be anti-ferromagnetically aligned. In addition, we have shown that the Mn $4p$ states have greater contribution to the hole states than $3d$ states, which is consistent with recently published theoretical results for bulk (Ga,Mn)As^{41,42}.

We have demonstrated that the holes are mostly localized in the closest proximity of the Mn-pair. Nevertheless, there are small contributions which come from the distant atoms indicating extended character of the holes. These observations strongly suggest that the Zener $p-d$ interaction⁴³ can also cause ferromagnetic coupling of the Mn-pairs at the surface, provided the magnetic moments of the Mn atoms forming the pair do not cancel each other (FM configurations).

Furthermore, our results clearly show that the local magnetic moments of Mn-ions polarize their surrounding always in such a way, that the Mn nearest neighbor As-atoms acquire the magnetic moments which are anti-ferromagnetically aligned to the Mn-spins.

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